Electronic Supplementary Information

(Z)-3-(Quinolin-2-ylmethylene)-3,4-dihydroquinoxalin-2(1H)-one derivatives:
AIE--active compounds with pronounced effects of ESIPT and TICT

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Instruments and measurements

All the reagents used were analytically pure and some chemicals were further purified by recrystallization or distillation. Melting points were determined by an OptiMelt automated melting point system. The $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were obtained on a Bruker Avance II DMX400 spectrometer using DMSO-$d_6$ as the solvent and tetramethylsilane as the internal standard. The absorption spectra were measured on a Shimadzu UV 2501(PC)S UV–Vis spectrometer and the fluorescence spectra were acquired on a Perkin-Elmer LS55 spectrophotometer. Quantum yields in THF were measured with quinine sulfate in 0.05M H$_2$SO$_4$ aqueous solution (Φ$_f$=0.55) or fluorescein in 0.1N NaOH aqueous solution (Φ$_f$=0.91) as the reference. The mass spectra were recorded on a HP 1110 mass spectrometer. Particle size is determined on a Beckman Coulter particle analyzer with 10 μM aggregate in THF/H$_2$O mixture (10 : 90, v/v) at 25 °C.

Computational details

The gas-phase geometries of the concerned complexes were optimized without any symmetry restrictions in singlet ground state using the density functional theory (DFT) method at the B3LYP level $[1]$. The 6–31G (d, p) basis set was selected for all the elements. The vibration frequency calculations were performed to ensure that the optimized geometries represented the local minima on the ground-state potential energy surface. All the calculations were carried out with the Gaussian 09 program package in the aid of the GaussView visualization program $[2]$.

The potential energy curves (PECs) of the ground state intramolecular proton transfer were calculated with the energies of the B3LYP/6-31G (d, p) fully optimized structures at the fixed N$_1$–H distances over the 0.8–2.2 Å. The PECs of the corresponding excited state intramolecular proton transfer were obtained by adding the TD-DFT/ B3LYP/6-31G (d, p) calculated vertical transition energy of the first singlet excited state to the energy.
of the ground state. The PECs of the ground state intramolecular torsion were calculated with energies of the B3LYP/6-31G (d, p) fully optimized structures at the fixed C₃-C₂-C₅-N₂ angle over the -90° to 270° range for 1a and 1b. The PECs of the corresponding excited state intramolecular torsion were obtained by adding the TD-DFT/B3LYP/6-31G (d, p) calculated vertical transition energy of the first singlet excited state to the energy of the ground state. The solvent effect on the ground and the first singlet excited state were executed with the polarizable continuum model (PCM).

**General procedure for preparation of compound 1a-d, 2e, 3a and 3a-Bn**

At room temperature, o-phenylenediamine (1 mmol), ethyl 2-oxo-3-(quinolin-2-yl)propanoate (1 mmol) or ethyl 2-oxo-3-(quinolin-2-yl)butanoate (1 mmol) and p-toluenesulfonic acid (0.1 mmol) are mixed in ethyl acetate (5 mL). The resulted mixture is refluxed for 24 h to offer the product as the solid. After the filtration, the solid is washed by ethanol and ether for several times followed by the recrystallization in the EtOH/THF mixture.

1a and 2a mixture: 75% overall yield, dark red powder, m.p. 215.6°C-216.3°C; EI-MS (70 eV) m/z (%): 347(M⁺, 100), 332(58), 319(15), 304(23), 275(15), 261(18), 168(15), 143(42), 128(18).

1a: ^1H NMR(400MHz, DMSO-d₆) δ 3.75(s, 3H), 3.89(s, 3H), 6.26(s, 1H), 6.71(s, 1H), 7.14(s, 1H), 7.31(d, J=8 Hz, 1H), 7.39(t, J=8 Hz, 1H), 7.65-7.70(m, 1H), 7.72-7.76(m, 1H), 7.97 (d, J=8 Hz, 1H), 8.12(d, J=8 Hz, 1H), 11.47(s, 1H), 13.71(s, 1H); ^13C NMR(100MHz, DMSO-d₆) δ 55.80, 56.21, 56.21, 59.82, 99.34, 102.08, 119.78, 121.28, 123.70, 124.33, 124.40, 124.65, 127.50, 129.88, 134.72, 140.72, 144.08, 145.15, 145.58, 145.78, 154.77, 156.36.

2a: ^1H NMR(400MHz, DMSO-d₆) δ 3.78(s, 3H), 3.83(s, 3H), 4.44(s, 2H), 6.79(s, 1H), 7.17(s, 1H), 7.51-7.57(m, 2H), 7.71(d, J=8 Hz, 1H), 7.89(d, J=8 Hz, 1H), 7.94(d, J=8 Hz, 1H), 8.28 (d, J=8 Hz, 1H), 12.30(s, 1H); ^13C NMR(100MHz, DMSO-d₆) δ 42.41, 55.71, 55.75, 56.92, 109.41, 122.42, 125.97, 126.60, 126.95, 127.80, 128.44, 129.41, 136.14, 145.72, 147.22, 151.09, 154.61, 155.95, 159.02.

1b: 83% yield, orange powder, m.p. 256.3-256.9 °C; EI-MS (70 eV) m/z (%): 347(M⁺, 100), 332(13), 303(15), 275(15), 203(8), 173(8), 156(10), 90(10); ^1H NMR(400MHz, DMSO-d₆) δ 3.91(s, 3H), 4.04(s, 3H), 6.35(s, 1H), 6.93(d, J=8 Hz, 1H), 7.05(s, 1H), 7.29(s, 1H), 7.33(d, J=8 Hz, 1H), 7.44(d, J=8 Hz, 1H), 7.57(s, 1H), 8.06(d, J=8 Hz, 1H).
Hz, 1H), 11.33(s, 1H), 13.20(s, 1H); $^{13}$C NMR(100MHz, DMSO-d$_6$) δ 55.59, 55.89, 95.67, 105.98, 106.92, 114.63, 114.90, 120.64, 120.93, 121.12, 123.21, 125.30, 126.41, 134.34, 135.12, 143.03, 148.62, 152.38, 155.07, 157.48.

1c: 88% yield, red powder, m.p. 245.5-246.2°C; EI-MS (70 eV) m/z (%) 287(M$^+$, 100), 258(91), 143(23), 129(25), 115(10), 101(8), 77(10); $^1$H NMR(400MHz, DMSO-d$_6$) δ 6.40(s, 1H), 6.99(t, J=8 Hz, 1H), 7.06-7.11(m, 2H), 7.44-7.51(m, 3H), 7.75(t, J=8 Hz, 1H), 7.87(d, J=8 Hz, 1H), 8.20(dd, J$_1$=8 Hz, J$_2$=4 Hz, 2H), 11.50(s, 1H), 13.73(s, 1H); $^{13}$C NMR(100MHz, DMSO-d$_6$) δ 94.35, 115.00, 115.21, 121.55, 123.31, 125.09, 125.14, 125.68, 126.35, 126.83, 127.55, 129.81, 135.67, 137.53, 145.74, 157.00, 157.05.

1d: 85% yield, red powder, m.p. 263.4-263.9°C; EI-MS (70 eV) m/z (%) 423(M$^+$, 100), 395(25), 308(20), 258(20), 211(22), 182(22), 168(32), 140(35), 128(57), 115(35), 79(23); $^1$H NMR(400MHz, DMSO-d$_6$) δ 3.76(s, 3H), 3.87(s, 3H), 6.38(d, J=8 Hz, 1H), 6.46(s, 1H), 6.90(t, J=8 Hz, 1H), 6.95(d, J=8 Hz, 1H), 7.05(s, 1H), 7.12-7.18(m, 2H), 7.49-7.55(m, 3H), 7.76(t, J=8 Hz, 1H), 7.87(d, J=8 Hz, 1H), 8.19(d, J=8 Hz, 1H), 8.23(d, J=8 Hz, 1H), 13.99(s, 1H); $^{13}$C NMR(100MHz, DMSO-d$_6$) δ 55.66, 55.74, 94.87, 112.27, 112.33, 115.60, 115.78, 120.77, 121.43, 123.46, 123.68, 125.17, 126.67, 126.91, 127.61, 129.00, 129.43, 129.92, 135.73, 137.55, 145.51, 148.88, 149.78, 156.74, 156.86.

2e: 72% yield, white powder, m.p. 164.7-165.4°C; EI-MS (70 eV) m/z (%) 301(M$^+$, 38), 286(100), 272(12), 156(50), 145(18), 128(40), 101(15), 90(18), 77(15); $^1$H NMR(400MHz, DMSO-d$_6$) δ 1.68(d, J=8 Hz, 3H), 4.93(q, J=8 Hz, 1H), 7.10 (m, 1H), 7.50-7.59(m, 3H), 7.67(t, J=8 Hz, 1H), 7.82(t, J=8 Hz, 2H), 7.93(d, J=8 Hz, 1H), 8.29(d, J=8 Hz, 1H), 12.3(s, 1H); $^{13}$C NMR(100MHz, DMSO-d$_6$) δ 17.98, 44.41, 115.20, 121.32, 123.05, 125.81, 126.54, 127.62, 128.45, 128.48, 129.21, 129.65, 131.48, 131.84, 136.25, 146.97, 154.21, 155.08, 162.37, 163.34.
At room temperature, the solution of 1a/2a mixture (1 mmol) in THF (2 mL) is irradiated at 254 nm under a low pressure mercury lamp for 48h. The solution is concentrated on a rotating evaporator and the residue is isolated by column chromatography on silica gel with petroleum ether (60-90°C)/acetone (3:1) as the eluent. The product 3a is the yellow powder in 88% yield.

3a: m.p. 185.2 °C (decomp.); EI-MS (70 eV) m/z (%) 361(M⁺, 52), 332(25), 204(18), 177(20), 150(18), 129(100), 120 (16), 101(31), 77(21); ¹H NMR(400MHz, DMSO-d₆) δ 3.84(s, 3H), 3.92(s, 3H), 6.91(s, 1H), 7.39(s, 1H), 7.78(t, J=8 Hz, 1H), 7.83(t, J=8 Hz, 1H), 7.98(d, J=8 Hz, 1H), 8.15(d, J=8 Hz, 1H), 8.20(d, J=8 Hz, 1H), 8.68(d, J=8 Hz, 1H), 12.72(s, 1H).

At room temperature, potassium carbonate (2 mmol) is added to the solution of 3a (1 mmol) and benzyl bromide (1.2 mmol) in acetone (2 mL), the resulted mixture is refluxing for 24h. After cooling to room temperature, the mixture is filtrated and the filtrate is concentrated on a rotating evaporator. The residue is isolated by column chromatography on silica gel with petroleum ether (60-90°C)/acetone (2:1) as the eluent. The product 3a-Bn is the orange powder in 81% yield.

3a-Bn: m.p. 217.3-218.6°C; EI-MS (70 eV) m/z (%) 451(M⁺, 43), 360 (95), 332(83), 316(20), 288(20), 218(22), 128(100), 101(30), 91(100), 77(15); ¹H NMR(400MHz, DMSO-d₆) δ 3.84(s, 3H), 3.86(s, 3H), 5.61(s, 2H), 7.08(s, 1H), 7.31-7.35(m, 1H), 7.40-7.42(m, 4H), 7.47(s, 1H), 7.79(td, J= 8 Hz, J= 1.6 Hz, 1H), 7.89(td, J= 8 Hz, J= 1.6 Hz, 1H), 7.94(d, J= 8 Hz, 1H), 8.14(d, J=8 Hz, 1H), 8.25(d, J=8 Hz, 1H), 8.70(d, J=8 Hz, 1H); ¹³C NMR (100MHz, DMSO-d₆) δ 44.23, 55.93, 56.23, 97.79, 111.02, 118.17, 126.77, 127.08, 127.62, 128.27, 128.78, 129.34, 129.49, 129.64, 130.89, 135.61, 138.24, 146.28, 146.45, 152.27, 152.69, 152.88, 153.47, 193.68.
Table S1  The difference of Gibbs free energy between the tautomers based on the calculations at DFT/B3LYP/PCM/6-31G(d,p) method in DMSO at 25°C and 1 atm.

<table>
<thead>
<tr>
<th>Compd</th>
<th>$\Delta G_1$(KJ/mol)</th>
<th>$\Delta G_2$(KJ/mol)</th>
<th>Cal. ratio $^d$ of 1 : 2</th>
<th>Exp. ratio $^e$ of 1 : 2</th>
<th>Cal. ratio $^d$ of 1N : 1T</th>
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<tr>
<td>a</td>
<td>3.217</td>
<td>2.884</td>
<td>3.2 : 1</td>
<td>3.3 : 1</td>
<td>3.7 : 1</td>
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<tr>
<td>b</td>
<td>7.003</td>
<td>17.572</td>
<td>1350 : 1</td>
<td>&gt; 50 : 1</td>
<td>16.9 : 1</td>
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<tr>
<td>c</td>
<td>4.452</td>
<td>17.543</td>
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<td>&gt; 50 : 1</td>
<td>6.0 : 1</td>
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<tr>
<td>d</td>
<td>5.593</td>
<td>9.989</td>
<td>57 : 1</td>
<td>&gt; 50 : 1</td>
<td>9.4 : 1</td>
</tr>
<tr>
<td>e</td>
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<td>-5.849</td>
<td>1 : 11</td>
<td>&lt; 1 : 50</td>
<td>- -</td>
</tr>
</tbody>
</table>

$^a$ Taking the Gibbs free energy of 1N isomer as the reference in a given product;

$^b$$\Delta G_1 = G_{1T} - G_{1N}$;

$^c$$\Delta G_2 = G_{2} - G_{1N}$;

$^d$ Estimated by the $\Delta G = -RT \ln K$ equation;

$^e$ determined by the $^1$H NMR
**Fig. S1** Photos of compounds in THF solution and coated on the inner wall of bottles under an ultraviolet lamp at 365 nm

**Fig. S2** The normalized absorption, excitation ($\lambda_{\text{em}}$ at 615 nm) and emission ($\lambda_{\text{ex}}$ at 480 nm) spectra of 1a in THF solution ($1 \times 10^{-4}$ M), PMMA film and solid state
Fig. S3  The normalized absorption, excitation ($\lambda_{em}$ at 600 nm) and emission ($\lambda_{ex}$ at 450 nm) spectra of 1b in THF solution ($1 \times 10^{-4}$ M), PMMA film and solid state.

Fig. S4  The normalized absorption, excitation ($\lambda_{em}$ at 600 nm) and emission ($\lambda_{ex}$ at 455 nm) spectra of 1d in THF solution ($1 \times 10^{-4}$ M), PMMA film and solid state.
Fig. S5  The normalized absorption and emission ($\lambda_{ex}$ at 317 nm) spectra of 2e
Fig. S6  (a) Fluorescence (excited at 450 nm) and (b) absorption spectra of 1c in 1×10^{-4} M THF/H2O mixture with varied water content; (c) fluorescence intensity of 1c depending on water fraction \( f_w (\%) \) in H2O/THF mixture; (d) photos under a hand-held ultraviolet lamp at 365 nm of 1c with varied volumetric fractions of water in THF.
Fig. S7  Size distribution by DLS of 1a (A), 1b (B), 1c (C) and 1d (D) aggregates (10 μM) in THF/H₂O (10:90, v/v) mixture solution
Fig. S8  Emission intensity ratio of $T^*/N^*$ isomers in 1a, 1c and 1d (2×10^{-5} M in THF) with varied excitation wavelength
Fig. S9  HOMOs and LUMOs of N-isomers in 1a-d
Fig. S10  Relative molecule total energy with varied bond length of N$_1$-H in 1aN by TD-DFT calculations at B3LYP/PCM/6-31G(d,p) level in THF.

Fig. S11  Relative molecule total energy with varied bond length of N$_1$-H in 1bN by TD-DFT calculations at B3LYP/PCM/6-31G(d,p) level in THF
Fig. S12  Relative molecule total energy with varied torsion angle of N\textsubscript{1}-C\textsubscript{3}-C\textsubscript{4}-C\textsubscript{5} in \textit{1cT*} by TD-DFT calculations at B3LYP/PCM/6-31G(d,p) level in THF.

Fig. S13  Relative molecule total energy with varied torsion angle of N\textsubscript{2}-C\textsubscript{5}-C\textsubscript{4}-C\textsubscript{3} in \textit{1cT*} by TD-DFT calculations at B3LYP/PCM/6-31G(d,p) level in THF.
Fig. S14  HOMO and LUMO of 1cT* in TICT state (90° torsion angle of N$_2$-C$_5$-C$_4$-C$_3$)

Fig. S15  Emission spectra of 1a ($2\times10^{-5}$ M in THF) with varied excitation wavelength
Fig. S16  Emission spectra of 1c (2×10⁻⁵ M in THF) with varied excitation wavelength

Fig. S17  Emission spectra of 1d (2×10⁻⁵ M in THF) with varied excitation wavelength
**Fig. S18**  Emission spectra of 1a (25 μM) with varied glycerol fraction in THF/glycerol mixture

**Fig. S19**  Emission spectra of 1b (25 μM) with varied glycerol fraction in THF/glycerol mixture
**Fig. S20**  Emission spectra of 1d (25 μM) with varied glycerol fraction in THF/glycerol mixture

**Fig. S21**  Absorption spectra of 1c in THF solution with different concentration
Fig. 22  Absorption spectra of 1c with different concentration in THF/H$_2$O(1:9, v/v) mixture
30

N
N
H
C
O
C
O
N
3
a-
Bn
(acetone co-crystal)

H₃CO
OCH₃

30
1b
References

